OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORTS

for

Grant or Contract N00014-89-J-1775

R & T Code 413n002 --- 01

Structure and Reactivity of Metal Clusters and Films

Larry L. Kesmodel

Indiana University

P.O. Box 1847
Bloomington, IN 47402

June 1, 1991

September 9, 1993

Ms. Mary P. Donnel
Procurement Technician
Department of the Navy
Office of Naval Research
Federal Building, Room 286
536 South Clark Street
Chicago, IL 60605-1588

RE: Grant # N00014-89-J-1775

Dear Ms, Donnel

In reference to your letter dated August 26, 1993 concerning the Final Technical. I am sending you one copy of the year end report, which Dr. Kesmodel filed in June, 1991.

The original expiration date of the grant was September 30, 1991. At this time Dr. Kesmodel submitted a proposal for additional funding, which was denied. He then asked for and received an extension of time. His technical monitor suggest that he let the year end report of June, 1991 be his final technical report.

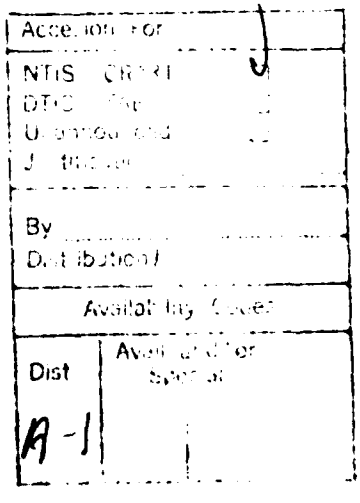
I am sending you a copy of that report in hopes it will be accepted by the technical people.

I have submitted copies to all parties mentioned in the grant document (including the DTIC).

If you have any questions please call me at 812/855-8691.

Sincerely,

Irene Adams
Contract and Grant Administrator
Indiana University



OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 413n002 --- 01
Contract/Grant Number: N00014-89-J-1775
Contract/Grant Title: Structure and Reactivity of Metal Clusters and Films
Principal Investigator: Larry L. Kesmodel
Mailing Address: Department of Physics
Indiana University
Bloomington, IN 47405

Phone Number: (812)855-0776 Fax Number: (812)855-5533
E-mail Address: BITNET: LKESMODE@IUBACS

a. Number of papers submitted to refereed journals, but not published: 2
b. Number of papers published in refereed journals (list attached)*: 1
c. Number of books or chapters submitted, but not yet published: _____
d. Number of books or chapters published (list attached)*: _____
e. Number of printed technical reports & non-refereed papers (list attached)*: 3
f. Number of patents filed: _____
g. Number of patents granted (list attached)*: _____
h. Number of invited presentations at workshops or professional society meetings: _____
i. Number of presentations at workshops or professional society meetings: _____
j. Honors/Awards/Prizes for contract/grant employees (list attached)*: _____
(This might include Scientific Society Awards/Offices,
Promotions, Faculty Awards/Offices)
k. Total number of Graduate Students and Post-Doctoral associates supported by at least 25% during this period, under this R&T project number:
Graduate Students: 4
Post-Doctoral Associates: 1
including the number of,
Female Graduate Students: _____
Female Post-Doctoral Associates: _____
the number of
Minority* Graduate Students: _____
Minority* Post-Doctoral Associates: _____
and, the number of
Asian Graduate Students: 2
Asian Post-Doctoral Associates: 1
l. Other funding (list agency, grant title, amount received this year, total amount, and period of performance)*

* Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

Enclosure (1)

Part I

a. Papers submitted to Refereed Journals

G.S. Glander, P. Akavoor and L.L. Kesmodel
HREELS Studies of Al Adsorption on Si(111), Physical Review B.

J.-S. Kim, M.H. Mohamed and L.L. Kesmodel
Vibrational Spectroscopy of Ordered Oxygen Adlayers on Ni/Cu(001) and Co/Cu(001) Thin Film Systems, Surface Science.

b. Papers Published in Refereed Journals

D.A. Hensley and L.L. Kesmodel, Application of HREELS to Model Catalysts: CO and C_2H_4 Adsorption on Pt/Al_2O_3, J. Phys. Chem. 95, 1368 (1991).

e. Technical Reports Published

ONR Technical Report No. 3 -- HREELS Studies of Al Adsorption on Si(111), G.S. Glander, P. Akavoor, and L.L. Kesmodel, May, 1991.

ONR Technical Report No. 4 -- Catalytic Activity of Model Pt/Al_2O_3 Catalysts: The Role of Chlorine, I. Boszormenyi, G.A. Somorjai and L.L. Kesmodel, May, 1991.

ONR Technical Report No. 5 -- Vibrational Spectroscopy of Ordered Oxygen Adlayers on Ni/Cu(001) and Co/Cu(001) Thin Film Systems, J.-S. Kim, M.H. Mohamed and L.L. Kesmodel.

k. Graduate Student and Postdoctoral Associates

Gregory W. Clark (Indiana University), graduate student
Prasad Akavoor (Indiana University), graduate student
Jae-Sung Kim (Indiana University), graduate student
Istvan Boszormenyi (University of California, Berkeley), graduate student
Dr. Taisei Nakayama (University of California, Berkeley), postdoctoral Associate

l. Other Funding

U.S. Department of Energy
High-Resolution Electron Energy Loss Studies of Surface Vibrations
Amount received year beginning 11/1/90 - $115,902
Total Amount - $365,408
Period of performance - 11/1/90-10/31/93

Part II

a. Principal Investigator - L.L. Kesmodel

b. Telephone (812)855-0776

c. Cognizant ONR Scientific Officer - Mark M. Ross

d. Project Description

The project involves new experimental studies of (i) the growth, structure and reactivity of metal clusters on oxide and semiconducting supports and (ii) the epitaxial growth and characterization of thin films on metal and semiconducting supports. The surface morphology of the clusters and films is to be investigated by scanning tunneling microscopy. The adsorption of hydrocarbons and carbon monoxide on the clusters is to be investigated by high-resolution electron energy loss spectroscopy (HREELS). The cluster reactivity is studied by a high-pressure/low pressure reaction cell. HREELS is also employed to study epitaxial film growth by examining the low frequency vibrational modes (phonons) associated with metal-metal and metal-semiconductor bonding.

e. Results During Last Year (1 June 1990 - 31 May 1991)

The chemisorption of carbon monoxide and ethylene on small platinum clusters was studied by HREELS and TEM (J. Phys. Chem. 95, 1368 (1991)). The clusters were formed by evaporation of platinum on thin aluminum oxide films and were found to average 1-2 nm in diameter. HREELS provided evidence of both π and di-σ type bonding of the ethylene at 165K. At higher temperatures (325K) the ethylene converted to ethylidyne ($\equiv$C-CH3), a species previously found on (111) platinum single-crystal surfaces.

The activity and regeneration of two model catalysts involving platinum and alumina were investigated (ONR Technical Report No. 4). One catalyst consisted of small platinum particles on alumina and the second involved alumina islands on a platinum foil. The presence of chlorine additive was found to improve the platinum activity for hydrocarbon conversion reactions.

Initial thin film studies of metals on silicon were begun by examining the case of aluminum on Si(111) in low coverage overlayer structures ($\sqrt{3}\times\sqrt{3}$, $\sqrt{7}\times\sqrt{7}$ and 7x7). HREELS and LEED were employed to characterize the film growth and the nature of the Al-Si low frequency vibrational modes. We reported new phonon modes for each structure, which are awaiting detailed theoretical interpretation (ONR Technical Report No. 3). Ultrathin films of the magnetic elements cobalt and nickel were grown on a Cu(001) substrate and characterized by HREELS and LEED. Oxygen chemisorption on these films was studied by HREELS and provided insight as to the thin film structures as a function of thickness. (ONR Technical Report No. 5). Clustering was evident for cobalt at low (1-2

monolayer) film thickness whereas nickel film growth appeared to be uniform.

Construction and testing of a UHV compatible STM was recently completed. The instrument has been tested on the Si(111)-7x7 structure and provides high quality atomic resolution images. The instrument will be used to characterize the structure of metallic clusters formed by in situ evaporation on semiconducting substrates.

f. Summary of Plans for Next Years Work

A brief outline of plans for next years work is listed below. A complete discussion will be given in the renewal proposal for the project.

The structure of metal clusters on semiconducting substrates will be investigated with scanning tunneling microscopy in ultrahigh vacuum. The system chosen will likely be platinum clusters on titanium dioxide. Spectroscopic STM studies are also planned to elucidate the electronic structure of the clusters. HREELS will be used to explore the chemisorption of various molecules on the clusters as well as to examine the electronic states of the clusters.

A study of the chemical activity of the clusters will continue in a collaboration with Professor Gabor Somorjai at the University of California. We are particularly interested in the ability of these clusters to catalyze hydrocarbon reactions.

g. Graduate Students and Post-Doctorals currently working on Project

Gregory W. Clark, Indiana University, graduate student
Prasad Akavoor, Indiana University, graduate student
Heui Seol Roh, Indiana University, graduate student
Istvan Boszormenyi, University of California, graduate student
Taisei Nakayama, University of California, postdoctoral associate

HREELS Studies of Dispersed Metal Clusters: CO and C_2H_4 Adsorption on Pt/Al_2O_3

* High-Resolution Electron Energy Loss Spectroscopy (HREELS) has been used to probe the chemisorption of carbon-monoxide and ethylene on platinum clusters.

* The clusters have a mean diameter of 1.5 nm and are dispersed on an aluminum oxide film. This serves as a model catalyst system for various important hydrocarbon reactions, such as ethylene hydrogenation.

* In HREELS, a scattered electron beam is analyzed to provide the energy losses associated with the vibrational modes of the adsorbed molecules.

* This work was one of the first uses of HREELS to examine the chemical bonding of hydrocarbons on metal clusters.

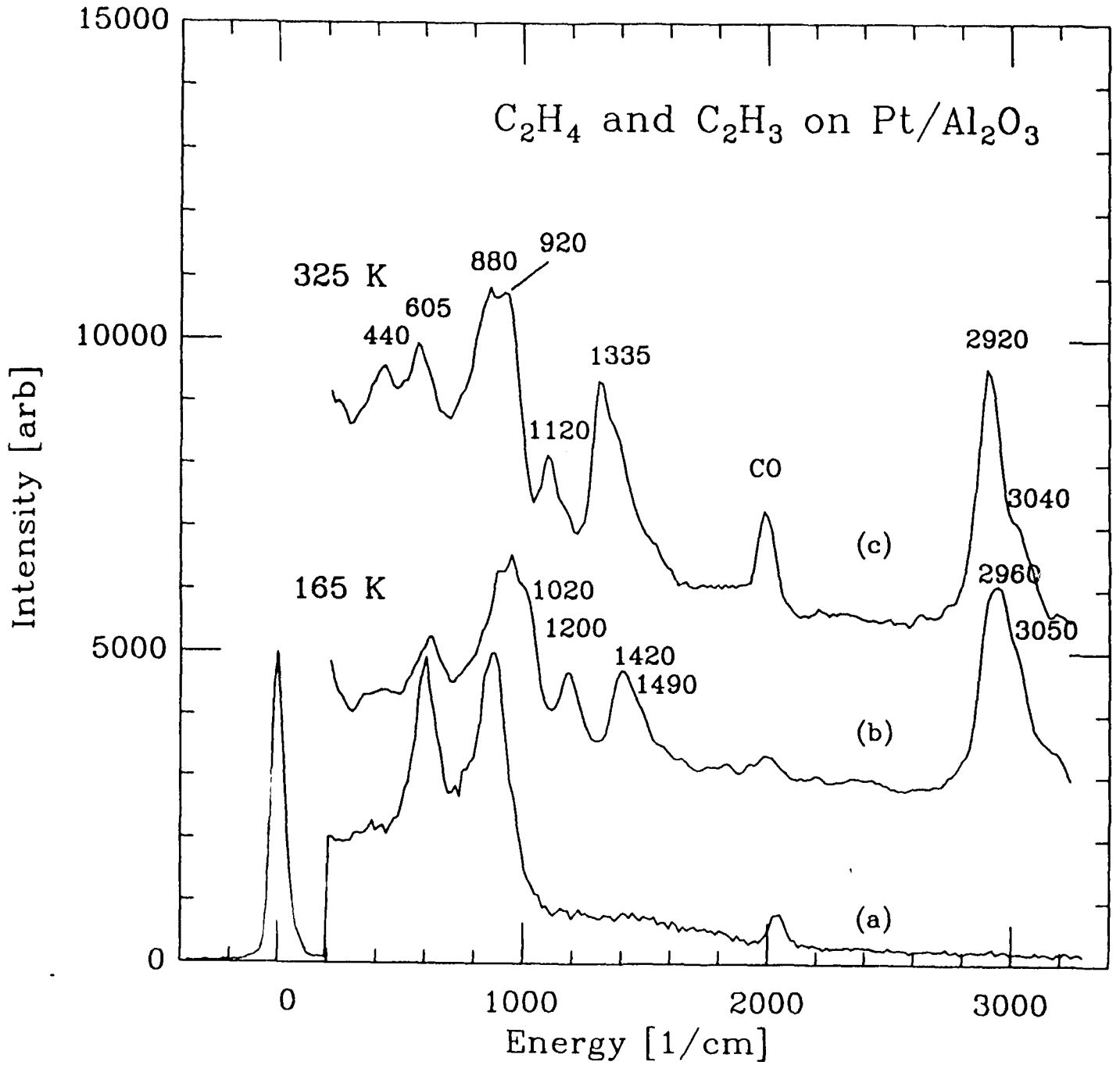
- Results

* As shown in the accompanying figure HREELS is able to resolve spectral features associated with
  (a) Clean model catalyst Pt/Al_2O_3

  (b) ethylene adsorbed at 165K

  (c) the product ethylidyne ($\equiv C\text{-}CH_3$) resulting from ethylene transformation near 325K

* This work demonstrates the capability of HREELS to probe the surface chemistry of small metal clusters.


C_2H_4 and C_2H_3 on Pt/Al_2O_3
325 K
165 K
440
605
880
920
1120
1335
CO
2920
3040
1020
1200
1420
1490
2960
3050
(a)
(b)
(c)
Intensity [arb]
Energy [1/cm]
15000
10000
5000
0
0
1000
2000
3000

We have used High-Resolution Electron Energy Loss Spectroscopy (HREELS) to characterize the chemisorption properties of metallic clusters. The clusters are formed by in-vacuo deposition of Pt onto an aluminum oxide film. The particles are found by TEM analysis to have a rather uniform size distribution with mean diameter 1.5 nm under the conditions used. HREELS was employed to characterize the vibrational spectra associated with ethylene (C_2H_4) adsorption and reaction. By analysis of the spectral positions two different types of ethylene bonding on the clusters could be discerned at 165K. Upon heating to 325K the ethylene converted to the ethylidyne ($\equiv C\text{-}CH_3$) species by virtue of new characteristic vibrational bands.